

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvement in or relating to Decontaminants or Cleansing Compositions

We, THE DOW CHEMICAL COMPANY, a corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a chemical composition useful in aqueous solution particularly for complexing of metal ions in the presence of hard water containing relatively large amounts of calcium.

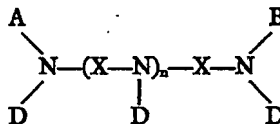
It is an object of the invention to provide a composition useful for dissolving metallic salt ingredients, such as radio-active constituents of solid phase materials.

Another object of the invention is to provide a detergent composition which, in aqueous solution, is suitable for washing surfaces for the removal of insoluble metallic residues or other metallic constituents, such composition being particularly useful in the presence of calcium.

Other object and advantages of the invention will in part be obvious and in part appear hereinafter.

This invention relates to a modification of the composition according to Specification 716,574 comprising a blend of from 1 to 5 parts by weight of an alkali metal orthophosphate or pyrophosphate detergent and 1 part by weight of an alkali metal, ammonium, or substituted ammonium salt of a synthetic polyamine polycarboxylic acid.

In a preferred embodiment of the present invention the detergent composition is of an alkaline nature which may contain alkali in the form of caustic alkali or carbonate, but contains an alkali metal orthophosphate or pyrophosphate in balanced proportion with certain polyamino polycarboxylic acid chelating agents, which correspond to the following generic formula:—



wherein A and B may be the same and are selected from the group consisting of β -hydroxy alkyl radicals, particularly those derived from alkyl radicals of low molecular weight, such as ethyl, propyl or butyl, and acetic and propionic acid residues, i.e., $-\text{CH}_2\text{COOM}$ and $-\text{CH}_2\text{CH}_2\text{COOM}$, wherein M is alkali metal, ammonium or substituted ammonium; D is selected from the group consisting of $-\text{CH}_2\text{COOM}$ and $-\text{CH}_2\text{CH}_2\text{COOM}$, wherein M is alkali metal, ammonium or substituted ammonium; and n is an integer having a value in the range from 0 to 5; X is a bivalent alkylene radical which adds 2—3 carbon atoms between the nitrogens; the proportions of said ingredients being in the weight ratio of five parts of the phosphate to one part of the polyamino polycarboxylic acid salt, varied to one part of the phosphate to one part of the polyamino polycarboxylic acid salt.

Typical compounds useful in the composition are the various alkali metal salts of the following:—

ethylenediaminetetraacetic acid;
monoethanolethylenediaminetriacetic acid,
diethanolethylenediaminediacetic acid,
the corresponding propanol and propionic acid compounds,

corresponding derivatives of polyamino polymers, such as those derived from diethylenetriamine, triethylenetetramine or tetraethylenepentamine.

A preferred composition comprises a blend of 2 parts by weight of tetrasodium pyrophosphate and 1 part by weight of ethylenediaminetetraacetic acid sodium salt.

In meeting chemical problems of detergency while using hard water, it is necessary to consider that one of the requisite conditions for the disappearance of a precipitate in contact

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with a solution is that the product of concentration of its ions must be smaller than the solubility product constant of the precipitate. Solution of the precipitate is favored if the concentration of one or both of its ions in the free state is reduced, and similarly, precipitation is inhibited. The synthetic polyamino polycarboxylic acids exercise a strong solubilizing effect by chelating the calcium ions present, which effect is considerably greater than that obtained by the use of sodium phosphate, tribasic. The calcium ion concentration which can be detected in a solution of the polyamino polycarboxylic acid is much lower than in the corresponding calcium pyrophosphate complex. Thus the polyamino polycarboxylic acids in proper proportions will solubilize calcium or magnesium pyrophosphate flocculant or crystalline solid phases.

Since the effectiveness of sodium pyrophosphate and sodium phosphate, tribasic, which are phosphate complexing agents, in preventing precipitation of insoluble calcium salts is limited by the insolubility of the double salts which they tend to form, we have found their effectiveness may be enhanced by cooperative action with the synthetic polyamino polycarboxylic acids.

As the concentration of Ca ions increases in hard water from 10 to 20 parts per million by weight, the amount of sodium phosphate, tribasic needed to keep it in solution increases about 5 times; from 20 to 40 parts per million Ca++, about 3 times; from 40 to 70 parts per million Ca++, about 4 times; and from 80 to 100 parts per million about 1½ times. It can be seen that increasing the Ca ion concentration in the water must be balanced by a disproportionately large relative increase in pyrophosphate ion, i.e., by a factor of 3 or 4 to 1. This suggests that 3 or 4 molecules of phosphate are involved in the binding of a single Ca ion. The synergistic action developed when synthetic polyamino carboxylic acid chelating agent is used with the phosphate in accordance with this invention can be partly attributed to the fact that binding a small amount of Ca by the chelating agent occurs at a 1:1 ratio. However, because of the high ratio of phosphate to Ca required, one mole of ethylenediaminetetraacetic acid, for example, saves many moles of the sodium pyrophosphate.

The greater the initial concentration of the Ca ion, the greater will be the excess of alkali metal phosphates needed to prevent precipitation and, hence, it soon becomes impracticable to continue the addition of the phosphates. It is to be noted that independent evidence indicates the Ca bound by the ethylenediaminetetraacetic acid involves a 1:1 ratio of the metal to organic sequestrant. The synergistic effect is manifested in the fact that one mole of ethylenediaminetetraacetic acid is equivalent to more than one mole of alkali metal phosphate, in fact 3 to 4 moles or more.

With tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, at 28° C. (T.S.P.P.) a limiting calcium concentration was found to exist above which it was impossible to prevent precipitation regardless of how great an excess of T.S.P.P. is present. This upper limit occurs between 55 and 60 parts per million of calcium ion. It is noteworthy that at this concentration the solution did not become turbid but a flocculent precipitate formed. This precipitate was calcium pyrophosphate, and after standing several days, it assumed a crystalline character. The precipitating ion in the test was the orthophosphate ion in a solution of trisodium phosphate. Table I shows the amount of T.S.P.P. required for a given calcium ion concentration in the presence of 0.25 percent $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$.

TABLE I.
Minimal quantities of TSPP necessary to prevent precipitation
Temperature 28° C.

In 0.25% $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$		
Calcium	$\text{Na}_4\text{P}_2\text{O}_7$ (anhyd.)	
ppm	ppm	
10	330	
20	800	
40	2120	
50	2660	
55	3000 limiting value	
50	3200	

The solid phase which is formed by calcium and pyrophosphate is flocculent but becomes crystalline on standing. At a mole:mole ratio of $\text{Na}_2\text{O}:\text{CaO}$ the salt is $\text{Na}_2\text{CaP}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$, or $\text{Ca}_2\text{P}_2\text{O}_7 \cdot \text{Na}_2\text{P}_2\text{O}_7 \cdot 8\text{H}_2\text{O}$. Up to 60 parts per million calcium ion corresponding to the minimal concentration of T.S.P.P. the solid phase approached the composition $7\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{Na}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$.

The third solid phase is a hydrate of a double salt, $5\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{Na}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$. X-ray and microscopic examination of the three solid phases show that the first two are individually identified, whereas the last is a mixture of the other two, richer in the former component.

In the presence of sodium carbonate and varying calcium ion concentrations the limiting concentration of T.S.P.P. is much lower than in the case of orthophosphate ion and a pronounced difference exists between 28° C. and 65° C. The 65° C. temperature is usually taken as the optimum for many industrial and household cleaning operations.

At 28° C. the upper limit on calcium ion content in water is 120 parts per million Ca ion. At this concentration precipitation of calcium pyrophosphate took place, regardless of the excess of T.S.P.P.

At 65° C. the upper limit was 40 parts per million Ca ion and the composition of the precipitate forming in the presence of Na_2CO_3 at the minimal concentration of T.S.P.P. was found to be $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$. Table II shows the limiting values of T.S.P.P.

TABLE II.
Minimal quantities of TSPP necessary to
prevent precipitation
in 0.10% Na₂CO₃ solution

5	Calcium ppm	Na ₄ P ₂ O ₇ (anhyd.) ppm
	10	25
	20	130
	40	400←limit 65° C.
10	80	1600
	100	2400
	120	— limit 28° C.

The suppressing action of T.S.P.P. on calcium ion in the presence of soap as a precipitating ion may now be considered. With an initial concentration of 40 parts per million of calcium ion, 4900 parts per million of T.S.P.P. was required to reduce the calcium ion to 10 parts per million; 2400 parts per million of T.S.P.P. was needed to reduce the calcium ion to 20 parts per million. The soap solution, pH 10, was turbid due to the salt effect of the high T.S.P.P. concentration.

Therefore, since T.S.P.P. has limiting complexing power toward calcium and/or magnesium ions, the presence of a given amount of ethylenediaminetetraacetic acid would be the deciding factor on the free calcium ion concentration and thereby effectively remove the

limiting barrier to its (T.S.P.P.) complexing power. The rates of reaction of ethylenediaminetetraacetic acid versus T.S.P.P. are such that it combines with its equivalent of calcium ion before T.S.P.P. can effectively complex any calcium ion.

It has been demonstrated that when ratios of 2.5 parts T.S.P.P.:1 part of ethylenediaminetetraacetic acid powder are employed the resulting composition has a complexing power greater than the additive values attributable to each component. For example:—

COMPOSITION No. 1.

25.0% EDTA Na₄
62.0% TSPP
13.0% H₂O
One gram of above formulation chelates 95.7 mg. of CaCO₃.

CALCIUM COMPLEXING VALUES OF COMPONENTS.

Since one gram EDTA Na₄ (commercial) complexes 204 mg. CaCO₃/g then the EDTA Na₄ content of 1 g. of formula 1 should complex 51.0 mg. CaCO₃.

Since 1 g. TSPP at pH 10 complexes 25 mg. CaCO₃/g, then the TSPP content of 1 g. of formulation 1 should complex 15.5 mg./CaCO₃.

SYNERGISTIC ACTIVITY.

But 1 gram of formulation 1 *actually* complexes 95.7 mg. CaCO₃.

25 g. EDTA Na₄ Comm. complexes - - 51.0 mg. CaCO₃
.62 g. TSPP Comm. complexes - - - 15.5 mg. CaCO₃

Theoretical complexing power - - - 66.5 mg. CaCO₃
66.5 mg. CaCO₃

29.2 mg. CaCO₃ Complexing power due to synergistic action

By varying the ratio of T.S.P.P. from 2.0 parts to 3 parts per one part ethylenediaminetetraacetic acid a useful mixture results that exhibits the synergistic action of ethylenediaminetetraacetic acid: T.S.P.P. combination and the limiting barrier on the complexing power of T.S.P.P. is effectively removed.

Other useful formulations are outlined as follows:—

75	Composition No. 2	Parts by weight
	*Ethanolethylenediaminetriacetic acid, sodium salt - - -	20
	T.S.P.P. - - - - -	40
80	Water - - - - -	5—10
	Composition No. 3	Parts by weight
	*Diethanolethylenediaminediacetic acid, sodium salt -	20
85	T.S.P.P. - - - - -	60
	Water - - - - -	5—10
	Composition No. 4	
	*Complexing agent - - -	25
	T.S.P.P. - - - - -	60
90	Water - - - - -	5—10

(*) In each composition, the complexing agent may be ethylenediaminetetraacetic acid, monoethanolethylenediaminetriacetic acid, diethanolethylenediaminediacetic acid, or mixtures thereof. Preferably they are used as their sodium salts. Compositions employing mixtures of the carboxylic acid compounds have the advantage that their maximum effectiveness can be spread over a somewhat wider pH range.

The compounds useful as the organic complexing agents are prepared by carboxymethylation of the corresponding diamine in accordance with U.S. Patent No. 2,407,645. The reaction product, together with side reaction products, is useful in the compositions in accordance with this invention. Following the carboxymethylation, the appropriate amount of orthophosphate or pyrophosphate may be added to the solution and the whole spray-dried.

Since T.S.P.P. has the greatest dispersing action on soil of any alkaline "builder", the one significant disadvantage to the useful life of T.S.P.P. in any formulation employed for

cleansing action is eliminated by combination with ethylenediaminetetraacetic acid in ratios above stated.

5 The action of ethylenediaminetetraacetic acid with sodium phosphate, tribasic (S.P.T.) is not as pronounced as with T.S.P.P. but S.P.T. also shows the same tendency to form solid phases with a calcium ion concentration greater than a calcium to phosphorus ratio of 1/4.

10 British Patent Specification No. 474,082 discloses, *inter alia*, a detergent composition comprising a washing agent (e.g. soap), a phosphate and an aminocarboxylic acid (or a salt thereof) containing more than one carboxylic acid group per amino nitrogen atom standing in α -position thereto, and containing also an organic radical, but free from an alkyl or cycloalkyl radical having 10 or more carbon atoms when the whole molecule contains only 2 carboxylic acid groups.

15 British Patent Specification No. 492,526 discloses, *inter alia*, a process for removing rust from rusty material by treating the material with a hot aqueous alkaline solution of the sodium salt of a water-soluble aminocarboxylic acid containing one or more basic nitrogen atoms which (or each of which) is bound to at least two organic residues each containing a carboxyl group in α -position to the nitrogen atom, to which there has been added a phosphate and a reducing agent capable of reducing ferric compounds to ferrous compounds.

20 British Patent Specification No. 568,000 discloses, *inter alia*, a process for restraining the precipitation of hardness-forming constituents from water and the formation of scale on surfaces in contact with the water by adding to the water 1—20 parts per million of ethylene-bis(iminodiacetic acid, or a water-soluble salt thereof, and a small proportion, e.g. 1—5 parts per million, of a soluble polyphosphate (preferably sodium hexametaphosphate).

25 In British Patent Specification No. 754,705 is described and claimed a detergent composition comprising a water-soluble anion-active or non-ionized surface-active agent, a salt of a polycarboxylated amine and either an alkanolamide of a fatty acid containing at least 8 carbon atoms in the molecule or a sulphonamide obtainable from an alkanolamine and an aliphatic monosulphochloride containing at

least 8 carbon atoms in the molecule. It is stated in this British patent, in the paragraph on page 1, line 88 to page 2, line 7, that this detergent composition may include additional ingredients, as for example, various sodium phosphate detergents. We hereby disclaim a detergent composition containing:—

(1) a blend of from 1 to 5 parts by weight of a sodium phosphate detergent and 1 part by weight of a salt of a polycarboxylated amine, and

(2) a water-soluble, anion-active or non-ionized surface-active agent, and

(3) either an alkanolamide of a fatty acid containing at least 8 carbon atoms in the molecule, or a sulphonamide obtainable from an alkanolamine and an aliphatic monosulphochloride containing at least 8 carbon atoms in the molecule.

What we claim, subject to the above disclaimer, is:—

1. Modification of the composition according to Specification 716,574 comprising a blend of from 1 to 5 parts by weight of an alkali metal orthophosphate or pyrophosphate detergent and 1 part by weight of an alkali metal, ammonium, or substituted ammonium salt of a synthetic polyamino polycarboxylic acid.

2. A composition in accordance with Claim 1, in which the pyrophosphate is tetrasodium pyrophosphate and the polycarboxylic acid salt is ethylenediaminetetraacetic acid sodium salt.

3. A composition in accordance with Claim 2, in which the pyrophosphate is present in the ratio of two parts by weight per part by weight of the ethylenediaminetetraacetic acid sodium salt.

4. A composition in accordance with Claim 1, in which the polycarboxylic acid salt is monoethanolethylenediaminetetraacetic acid sodium salt.

5. A composition in accordance with Claim 1, in which the polycarboxylic acid salt is diethanolethylenediaminediacetic acid sodium salt.

6. Modification of the composition according to Specification 716,574, substantially as hereinbefore described with reference to any one of composition Nos. 1—4.

THE DOW CHEMICAL COMPANY,

Per: Boulton, Wade & Tennant,
111/112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.